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ORIGINAL PAPER

Fluidity and heat resistance of polyphenylene oxide compounded with crystalline plasticizer

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Abstract Polyphenylene oxide (PPO) was compounded with bisphenol-S on Haake Rheometer and the torque during mixing was recorded. The dynamic properties of the PPO compounds were analyzed with dynamic mechanical analyzer and the phase structure was examined with transmission electron microscope and differential scanning calorimeter. The effect of the added bisphenol-S on the motion of the chain segments, the fluidity, stiffness, and heat resistance of the PPO were studied. At mixing temperature 280 °C the Bisphenol-S melted and dissolved in PPO; as the compounds cooled and solidified after molding the bisphenol-S precipitated and recrystallized, presented as 40 nm particles in the PPO matrix. Bisphenol-S reduces the viscosity of PPO melts but does not deteriorate the stiffness and heat resistance of PPO materials. Bisphenol-S is more efficient than polystyrene to reducing the viscosity of PPO. At 5 parts of bisphenol-S, the torque decreased 35%.

Keywords Poly(phenylene oxide) · Melt viscosity · Heat distortion temperature · Phase structure · Plasticizer

Introduction

Plasticizer is a type of additive that is used for plastics to achieve good fluidity and flexibility [1–3]. The molecules of the added plasticizer are dispersed in polymeric

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matrixes as separating molecules. They reduce the internal friction of polymeric chains, thereby, reducing the viscosity of polymer melts. However, at the same time as they reduce the viscosity, they reduce the modulus and heat resistance as well. The modulus and heat distortion temperature of the plasticized polymers descends with the increasing of plasticizer. Plasticizers are seldom used in thermoplastic engineering plastics though they are widely used in industrials. But the actual situation is that many thermoplastic engineering plastics are confronted with difficulties in melt processing, such as polyphenylene oxide (PPO) [4], polysulfone (PSF) [5, 6], and polyetheretherketone (PEEK) [7].

PPO is an amorphous engineering plastic whose molecules are composed of 2,6-dimethyl phenyl joined by C–O ether bonds. The methyl groups on the benzyl rings hinder the rotation of the chain elements around the ether bonds and the PPO molecules are of rigid chains. Due to the feature of the rigid chains, PPO possesses high melt viscosity. It is difficult for melt processing without modification [8–11]. In industrials, virginal PPO resin is normally blended with some amounts of polystyrene (PS) so as to reduce the viscosity and improve the fluidity. Higher the PS content, higher the fluidity. But PS is miscible with PPO; the PS reduces not only the melt viscosity of PPO but also the glass transition temperature. Consequently, the heat distortion temperature of the resultant blends deteriorates compared to that of the neat PPO. On the other hand, because of the macromolecular features PS is not very efficient to reduce the viscosity. The improvement in the fluidity is limited, especially in the case that high heat resistance is to be maintained and the PS content has to be low.

Syndiotactic polystyrene (S-PS) is a crystalline polymer and has a melting point about 270 °C [12]. The working temperature of S-PS is much higher than that of atactic PS. It was expected [13] that the processing properties of PPO would be improved, while the heat distortion temperature would not be affected when S-PS was incorporated into PPO. However, the fact is that when S-PS was added into PPO, the resultant blends exhibited only one glass transition. The glass transition temperature of S-PS-modified PPO was composition dependent and shifted towards low temperature as occurred in atactic PS-modified PPO. No S-PS crystallites had been identified in the blends with DSC and WAXD at all. Because S-PS possesses the same composition as atactic PS, it is miscible with PPO. S-PS did not precipitate and recrystallize in the blend after molding. In a research work about PSF modification [5], a crystalline oligomer, poly(bisphenol-A), was blended with PSF to reduce the viscosity of PSF melt. The blend also exhibited one composition dependent glass transition. The poly(bisphenol-A) did not recrystallize, the heat distortion temperature of modified PSF decreased.

Principally, the phase structures of a mixture are related to the factors of both thermodynamics and kinetics, and the thermodynamic factors are temperature dependent also. The mixing free energy of a system varies with temperature; a mixture may alternate from soluble to insoluble as temperature changes. For polymeric systems, although the mixing free energy varies with temperature, the corresponding phase structure may be retarded by the kinetic factor because of the macromolecular features. The morphology of multiphase polymers is strongly dependent on the processing conditions [14, 15] and heat history [16]. However, for low molecules, the response of morphology to thermodynamic variation should be much quicker. It should be possible that some organic crystallites fuse and dissolve in a polymeric melt at elevated temperature, but precipitate and recrystallize as temperature decreases. The organic crystallites may functions as plasticizers but with phase transition. Such substances may reduce the viscosity of the polymeric melt in processing but not deteriorate the heat resistance of the resultant materials. Bisphenol-S (BP-S) is an organic crystallite with a melting point of 250 °C. It has been incorporated into virginal PPO in this work; the fluidity and glass transition temperature of the PPO compounds were measured and the phase structures were examined.

Experiment

Raw materials

Poly(phenylene oxide) (PPO) used in this work is a virginal PPO powder, provided by General Electric Plastics. Atactic PS is a commercial product for general purpose (Dow Styron 666D). According to the manufacturer's literature, the melt flow index of the resin is 8 g/10 min at 200 °C. Bisphenol-S (BP-S) was purchased from Aldrich. The purity is above 98% and the melting point is about 250 °C. The BP-S was used as received without further purification before compounding.

Mixing and molding

PPO was blended with BP-S on Haake Rheocord 9000 equipped with Mixer 600. The temperature of the mixer wall was set at 280 °C and the rotators operated at 20 rpm. The neat PPO powder was first dry-mixed with desired BP-S, and then 63 g of the powder mixtures were charged into the chamber of the mixer and the torque was recorded. The value at equilibrium state was taken as the measurement for the fluidity of the compounds. After mixing for 15 min, the compounds were discharged and compression molded into 2 mm thick plates in a hot press at 280 °C. For comparison, PPO was blended with PS on the Haake Mixer at 280 °C at the same charging coefficient of the chamber.

Dynamic mechanical analysis

Dynamic mechanical analysis of the PPO compounds was performed on TA DMA 983 Dynamic Mechanical Analyzer. The compression-molded specimens were cut into strips about 4 mm wide and mounted on the specimen clamps of the DMA instrument. The span between the clamp arms was fixed at 30 mm and the instrument was operated at a frequency of 3.5 Hz and oscillation amplitude of 0.2 mm. Temperature scanned from 40 to 250 °C at a heating rate of 1 °C/min, the store modulus and loss tangent against temperature were reported. The temperature at loss tangent peak was taken as the glass transition temperature for the sample. The distortion temperature was identified on the store modulus curve, at which the modulus decreased 25% from the value at 40 °C. The distortion temperature was closed to the up deflection point of the curve, after which the modulus descended faster and faster.

Differential scanning calorimeter analysis

The fusion behaviors of the PPO compounds were analyzed with differential scanning calorimeter (DSC). About 10 mg of sample chips were put in aluminum sample pans and mounted in NETZSCH 204 F1 DSC. Under nitrogen stream of 20 mL/min, the specimens were heated from 50 to 300 °C at a scanning rate of 10 °C/min. The recorded heat flow against temperature was reported.

Transmission electron microscope examination

The sample bars were trimmed first with razor by hand and then with glass knife on a Reichert-Jung Ultracut R microtome. After about 500 nm thick materials were removed from the top of the specimens, slices about 60 nm thick were sectioned with a diamond knife on Ultracut R microtome at 1.0 mm/s and ambient temperature. The ultra thin sections were mounted on 300 mesh copper grids and dried in a desiccator for 4 h at least, and then were stained for about 30 min in ruthenium tetroxide vapor generated in situ [17–19]. The transmission electron microscopy (TEM) examination of the slices was performed on JEOL JEM-100CX II TEM. An accelerating voltage of 80 kV was adopted.

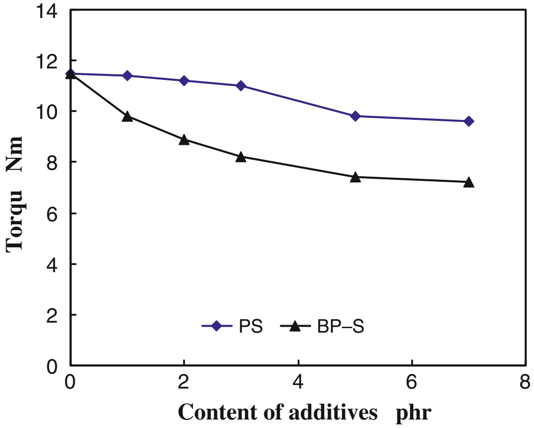
Results and discussions

Equilibrium torque of PPO melts

Virginal PPO is difficult for melt processing because of its molecular rigidity. Neat PPO powder did not coalesce in Haake Mixer until 250 °C; the temperature should be increased to 280 °C, the PPO powder could coalesce to each other and flow smoothly in the mixer with the agitation of the rotators. At 280 °C, the torque of neat PPO melt at equilibrium state was measured to be about 11.5 Nm.

At 280 °C, BP-S melted and dissolved in PPO under the agitation of the rotators; it reduced the viscosity of the PPO melt. Figure 1 shows the torque of PPO after incorporated with different amounts of BP-S at 280 °C. At 1 part of BP-S, the torque decreased from 11.5 to 9.8 Nm, being 15% lower than that of the neat PPO. At 5 parts of BP-S, the torque decreased to 7.4 Nm, only about 65% of the torque of the neat PPO. Compared to PS, which is popularly used in industrials for improving the fluidity of PPO, BP-S possesses higher plasticizing capacity. At the same content, BP-S resulted in a much lower torque value than PS; the curve of the torque against content for BP-S is below that for PS (ref. Fig. 1). When 7 parts of PS was blended, the torque was as high as 9.8 Nm, which is equivalent to the torque value of PPO compounded with 1 part of BP-S only.

Fig. 1 Torque variation of PPO with added bisphenol-S (BP-S) and polystyrene (PS) during mixing at 280 °C



Glass transition of PPO compounds

Due to the rigidity of the molecular chain, PPO is in glass state at ambient temperature and the motion of the chain segments is frozen. Figure 2 shows the spectrum of the neat PPO. The loss tangent of the neat PPO remained at relative low value as temperature was below 190 °C. Afterwards, the motion of the chain segments was initiated and the loss tangent ascended faster and faster. After a maximum it descended. From the loss tangent curve the glass transition temperature has been determined to be 209 °C.

The neat PPO exhibited a store modulus of about 2.6 GPa at 40 °C. The modulus could maintain above 2.0 GPa until 195 °C. After this point, the modulus descended faster and faster which means that more and more chain segments were activated as temperature increased further. From the curve of the store modulus, the distortion temperature was determined to be 195 °C, at which the modulus had decreased

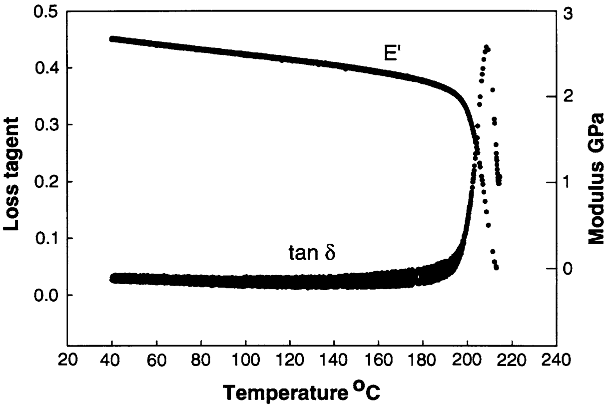


Fig. 2 DMA spectrum of neat PPO at 3.5 Hz

25%. This temperature is very close to the reported heat distortion temperature of neat PPO.

The effect of the added BP-S on the motion of PPO chain segments has been analyzed. Figure 3 shows the DMA spectra of the PPO/BP-S compounds. The DMA spectra of the PPO compounds were similar to that of neat PPO. On the loss modulus spectra, only one loss tangent peak could be observed for each sample. The determined glass transition temperatures are almost identical to that of neat PPO and they float between 209 and 210 °C. BP-S appears to not affect the motion of PPO chain segments. Anyway, the loss curve broadened towards the low temperature a little. The DMA spectra in Fig. 3 indicate that BP-S does not affect the motion of the chain segments seriously though it reduces the viscosity of PPO melt as plasticizer.

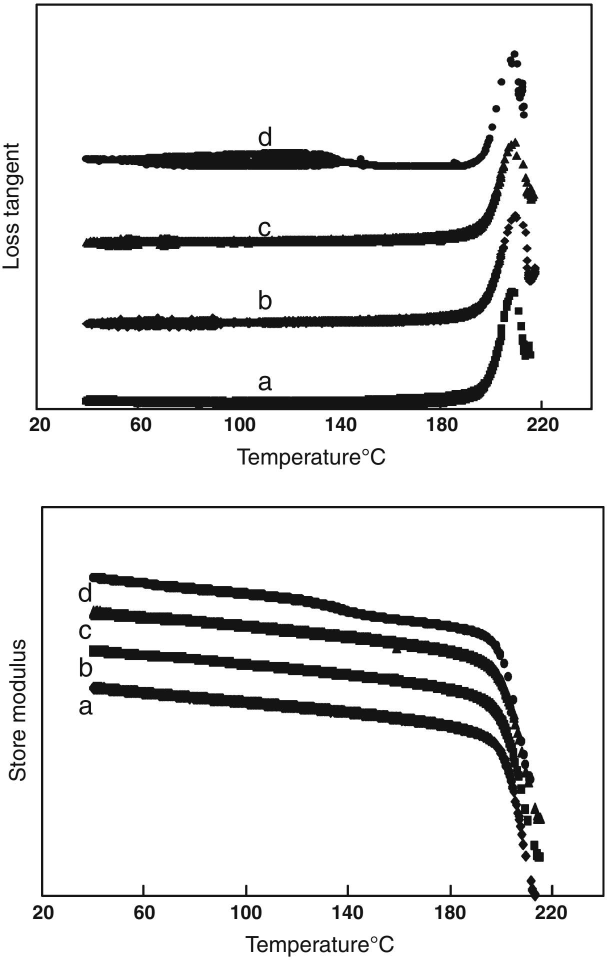


Fig. 3 DMA spectra of PPO compounded with BP-S. (*a*) neat PPO and PPO compounded with BP-S, (*b*) 1 phr, (*c*) 3 phr, and (*d*) 7 phr

Figure 4 shows the measured distortion temperature of PPO after being compounded with different amount of BP-S. As 1 part of BP-S was added, the distortion temperature of the compound was measured to be about 191 °C, being about 4 °C lower than that of the neat PPO. As the amount of BP-S increased further, the distortion temperature did not go down continually but floated around this temperature till 7 parts of BP-S. For PS that is being incorporated in most of the commercial PPO granules, the distortion temperature decreased almost linearly with increasing PS content. At 7 parts of PS the heat distortion temperature is below 180 °C, being 15 °C lower than that of neat PPO. While the torque is as high as 9.8 Nm still, only 15% lower than the torque of neat PPO.

Phase structure of PPO compounds

Figure 5 shows the DSC curve of the PPO incorporated with 5 parts of BP-S. The DSC graph exhibits a sharp endothermal peak at temperature about 250 °C. The endothermal peak is closed to the melting point of BP-S. PPO is non-crystalline polymer; the endothermal peak should be attributed to the fusion of BP-S crystallites in the sample. The DSC curve implies that dissolved BP-S will precipitate and crystallize in the PPO matrix after molding.

The morphology of the PPO compounded with 5 parts of BP-S was examined under TEM. PPO is an amorphous polymer, and no phase features have been observed under TEM except for some knife marks on the slices. However, on the slices of the PPO compound some dark dots were observed, as shown in Fig. 6. The sizes of the dots ranged from about 10–40 nm and their boundaries were blunt. In addition, the darkness varied for these dots; normally, the large ones appeared darker. The dark dots should be for BP-S in the compound. However, the volume of the dark dots seems to be larger than 5%. The dots may represent for the domains rich in BP-S, i.e., the BP-S domains that contain a few PPO chain elements, especially in the interfacial layers. Because the examined slices were about 60 nm thick, the large dark dot should be an intact BP-S rich domain, while the small one

Fig. 4 Variation of distortion temperature of PPO with added bisphenol-S (BP-S) and polystyrene (PS)

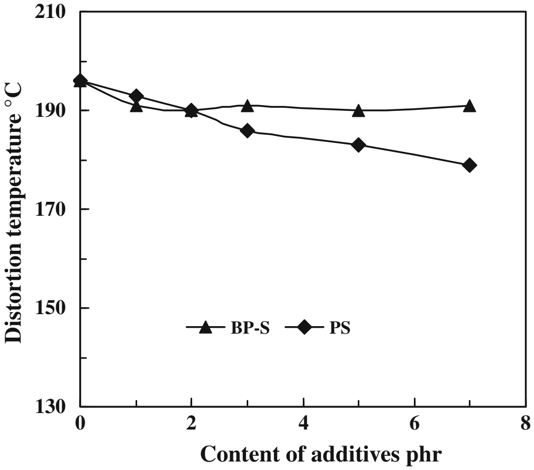


Fig. 5 Fusion curve of PPO compounded with 5 parts of BP-S

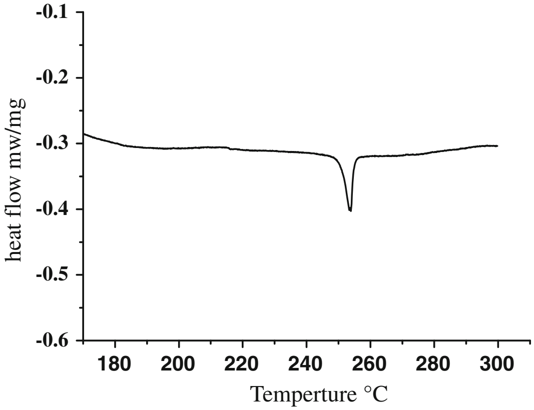
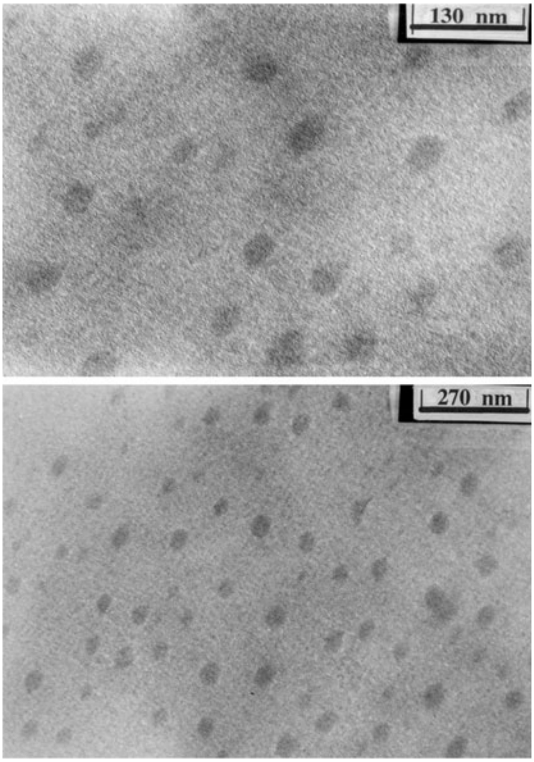


Fig. 6 TEM photograph of PPO compounded with 5 parts of BP-S



should be for the domains that had been cut through during section. Anyway, TEM examination revealed that the BP-S presents as BP-S rich domains with diameter about 40 nm in PPO matrix.

At mixing and molding temperature, perhaps, BP-S dissolved in PPO melt. It functioned as plasticizer and reduced the viscosity and the torque. During cooling process after molding, the solubility of BP-S might decrease and aggregate together as the temperature decreased; because the melting point of BP-S is 250 °C, and the glass transition of PPO occurs at temperature around 210 °C. As the PPO compounds cooled to temperature between the melting point and glass transition temperature, the dissolved BP-S molecules precipitated and recrystallized, generated BP-S crystals in the PPO matrix. In the molded specimens, the BP-S does not affect the motion of PPO chain segments seriously. Nevertheless, BP-S has induced a shift in the incipience of glass transition to low temperature compared to the neat PPO, the distortion temperature decreased a little. However, the amount of the shift is small, and the T_g incipience seems to be constant with increasing BP-S content (ref. Fig. 4). This implies that a few isolated BP-S molecules exist in PPO, most likely in the interfacial layers between the BP-S domains and PPO matrix.

Normally, PPO is incorporated with PS to improve the fluidity. At the same time to improve the fluidity, PS reduces the glass transition temperature and heat resistance of PPO. The present results are of most interesting. BP-S can reduce the viscosity of PPO greatly at processing temperature but does not affect the heat resistance. After molding BP-S molecules can precipitate and form fine crystalline phases in the PPO matrix; thus, the BP-S does not reduce the stiffness and heat resistance of PPO seriously. These results clearly demonstrate that it is possible to get some substances that can function as plasticizer with phase transition; thus, they can reduce the viscosity of polymeric melts at processing temperature but does not deteriorate the heat resistance of the plastics in working conditions. For PPO resin, the ideal phase transition plasticizer should:

1. possess melting point above the glass transition temperature of PPO;
2. be soluble in PPO at molding temperature and become insoluble as temperature decreases towards the glass transition temperature of PPO;
3. be stable at the processing temperature of PPO.

Conclusions

Bisphenol-S is miscible with PPO at 280 °C. It will precipitate and recrystallize as the PPO compounds solidify after molding. Bisphenol-S exists as domains in PPO matrix with diameter about 40 nm. Hence, bisphenol-S is able to reduce the viscosity of PPO melt but does not reduce the stiffness and heat resistance of PPO materials seriously at the content up to 7 parts. Bisphenol-S is more efficient than PS to reducing the viscosity of PPO melt. At 5 parts of bisphenol-S, the torque decreases 35% while the distortion temperature decreases 5 °C only. Furthermore, the distortion temperature does not decrease further with increasing bisphenol-S content up to 7 parts.

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